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⑥ EXCIPLEX LASER KINETICS

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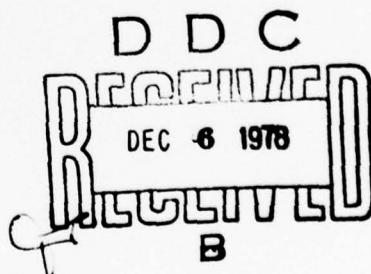
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19. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Measurements of the rates of collisional quenching of HgCl* and HgBr* ( $B^2\Sigma^+$ ) <sub>1/2</sub> by rare gases and halogenated molecules are reported in this paper. HgCl* and HgBr* fluorescence is produced by photolyzing HgCl <sub>2</sub> and HgBr <sub>2</sub> respectively using Xe <sub>2</sub> * radiation. A background pressure of [Xe] > 100 torr ensures that the HgCl* and HgBr* is vibrationally relaxed. The rates are derived by using a modified Stern-Volmer analysis and estimated lifetime of the HgCl* and HgBr* ( $B^2\Sigma^+$ ) <sub>1/2</sub> states of 29 nsec and 23 nsec, respectively.		

B<sub>2</sub>Sigma<sup>+</sup> 1/2

## REPORT SUMMARY

Efficient scaling of mercury monohalide lasers to high average power requires knowledge of the processes responsible for the formation and quenching of the upper laser level. From the formation kinetics one can determine the upper state production efficiency. The quenching kinetics enables one to choose the appropriate mix and determine the laser saturation flux. These processes together with the upper and lower level relaxation in XeF have been studied this year at AERL.

In this report we outline the investigation involved in determining the quenching of  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) and  $\text{HgBr}^*$  ( $B^2\Sigma_{1/2}^+$ ) which are the upper levels of these laser systems. Collisional quenching by the rare gases and various halogen donor candidates was measured using a Xe flashlamp to photolytically pump  $\text{HgX}_2$  ( $X = \text{Cl, Br}$ ) salts to produce  $\text{HgX}^*$  B state.

Measurements were made of rates of quenching of  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) by He, Ne, Ar, Kr, Xe,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{HCl}$ , and  $\text{CCl}_4$  at pressures below 3000 torr and of  $\text{HgBr}^*$  ( $B^2\Sigma_{1/2}^+$ ) by He, Ar, Xe,  $\text{N}_2$ ,  $\text{Br}_2$ ,  $\text{CF}_3\text{Br}$ ,  $\text{CCl}_3\text{Br}$  at pressures below 1000 torr.

Lasing and fluorescence measurements at AERL on the  $\text{HgCl}^*$  system indicate that none of the measured rates is fast enough to explain the results. A possible candidate which we have identified that could rapidly quench  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) is Hg. The rate of quenching of  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) by Hg is an important rate which should be measured.

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## TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
Report Summary	1
List of Illustrations	5
I. INTRODUCTION	7
II. DEVICE FOR QUENCHING STUDIES ON RARE GAS AND METAL HALIDE EXCITED COMPLEXES	13
III. TWO BODY COLLISIONAL QUENCHING KINETICS OF $HgCl^*$ ( $B^2\Sigma$ )	21
Acknowledgments	29
References	31

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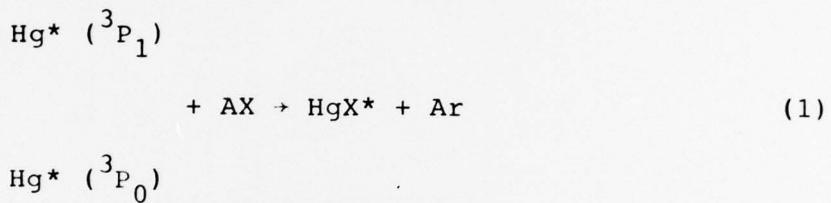
<u>Figure</u>		<u>Page</u>
1	Schematic Diagram of Apparatus for HgX* Formation Experiments	8
2	Schematic Diagram of Experimental Apparatus for HgX* Quenching Experiments	16
3	Schematic Diagram of Xe Flashlamp Pulse Circuit	17
4a	Measured HgCl* Emission with $[HgCl_2] = 50 \mu m$	18
4b	Measured HgCl* Emission with $[HgCl_2] = 50 \mu m$ and $[Xe] = 200 \text{ Torr}$	18
5	Measured Data for HCl Quenching HgCl*	27

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## I. INTRODUCTION

Efficient scaling of mercury monohalide lasers to high average power requires knowledge of the processes responsible for the formation and quenching of the upper laser level. From the formation kinetics one can determine the upper state production efficiency. The quenching kinetics enables one to choose the appropriate mix and determine the laser saturation flux.

An apparatus has been set up in which measurements of the formation processes viz.



(where X = Cl, Br) are presently being made. A schematic diagram of the apparatus is shown in Figure 1.

Quenching measurements have been made in a second device. In this device  $\text{HgCl}^*$  is photolytically produced by optically exciting  $\text{HgCl}_2$ . The same apparatus can be used to excite other metal and rare gas complexes. The device is small, allowing rapid screening using repetitive pulsing and signal averaging techniques. A detail description of the apparatus appears in Section II.

Measurements of the rates of collisional quenching of  $\text{HgCl}^*$  ( $\text{B}^2 \Sigma^+_{1/2}$ ) by He, Ar, Xe, N<sub>2</sub>, Cl<sub>2</sub>, HCl and CCl<sub>4</sub> are described in

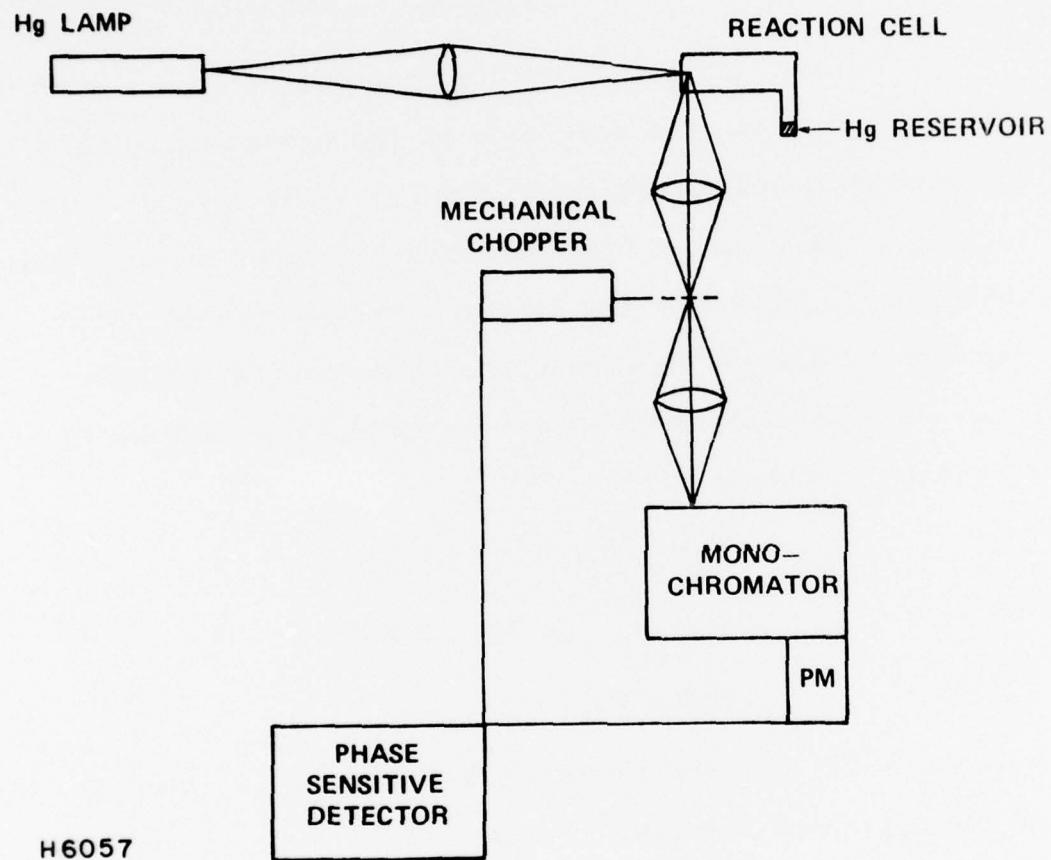


Figure 1 Schematic Diagram of Apparatus for  $\text{HgX}^*$  Formation Experiments

Section III. Steady state measurements are made of  $\text{HgCl}^*$  fluorescence by photolyzing  $\text{HgCl}_2$  using  $\text{Xe}_2^*$  radiation. A background pressure of  $[\text{Xe}] \geq 100$  torr ensures that the  $\text{HgCl}^*$  is vibrationally relaxed.  $\text{He}$ ,  $\text{Ar}$  and  $\text{N}_2$  exhibited small quenching rates while  $\text{Xe}$  did exhibit a three body dependence for high pressure. These rates are derived by using an estimated  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) lifetime of 29 nsec.

A significant number of measurements has been made of  $\text{HgCl}^*$  and  $\text{HgBr}^*$  quenching. Tables I and II summarize the results of these measurements.

TABLE I  
 $\text{HgCl}^*$  QUENCHING  
 (Assuming  $\tau_{\text{HgCl}^*} = 29$  nsec)

<u>Q</u>	$k_Q \tau$	$k_Q$
He	$9 \times 10^{-22} \text{ cm}^3$	$3.1 \times 10^{-14} \text{ cm}^3/\text{sec}$
Ne	$7.3 \times 10^{-22} \text{ cm}^3$	$2.5 \times 10^{-14} \text{ cm}^3/\text{sec}$
Ar	$1.1 \times 10^{-21} \text{ cm}^3$	$3.8 \times 10^{-14} \text{ cm}^3/\text{awx}$
Kr	$1.6 \times 10^{-21} \text{ cm}^3$	$5.6 \times 10^{-14} \text{ cm}^3/\text{sec}$
Xe	$6.9 \times 10^{-21} \text{ cm}^3$	$2.4 \times 10^{-13} \text{ cm}^3/\text{sec}$ (2 body)
Xe	$2.7 \times 10^{-40} \text{ cm}^6$	$9.2 \times 10^{-33} \text{ cm}^6/\text{sec}$ (3 body)
$\text{N}_2$	$1.4 \times 10^{-21} \text{ cm}^3$	$4.7 \times 10^{-14} \text{ cm}^3/\text{sec}$
$\text{Cl}_2$	$3.8 \times 10^{-18} \text{ cm}^3$	$1.3 \times 10^{-10} \text{ cm}^3/\text{sec}$
HCl	$2.5 \times 10^{-18} \text{ cm}^3$	$8.6 \times 10^{-11} \text{ cm}^3/\text{sec}$
$\text{CCl}_4$	$3.5 \times 10^{-18} \text{ cm}^3$	$1.2 \times 10^{-10} \text{ cm}^3/\text{sec}$

TABLE 11

HgBr<sup>\*</sup> QUENCHING FOR  
<sup>1</sup>HgBr<sup>\*</sup> = 23 nsec

	<u><math>k_Q</math></u> <u>(cm<sup>3</sup>)</u>	<u><math>k_Q</math></u> <u>(cm<sup>3</sup>/sec)</u>
He	$< 1.5 \times 10^{-21}$	—
Ar	$< 1.5 \times 10^{-21}$	—
Xe	$7.1 \times 10^{-21}$	$3.1 \times 10^{-13}$
N <sub>2</sub>	$< 1.5 \times 10^{-21}$	—
Br <sub>2</sub>	$6.9 \times 10^{-18}$	$3 \times 10^{-10}$
HBr	$3 \times 10^{-18}$	$1.3 \times 10^{-10}$
CF <sub>3</sub> Br	$2.1 \times 10^{-18}$	$9 \times 10^{-11}$
CCl <sub>3</sub> Br	$4.4 \times 10^{-18}$	$1.9 \times 10^{-10}$

### II. DEVICE FOR QUENCHING STUDIES ON RARE GAS AND METAL HALIDE EXCITED COMPLEXES

A new class of molecular lasers has been developed over the past few years -- the exciplex lasers. These lasers include the rare gas halides of which KrF,<sup>(1)</sup> XeF<sup>(2)</sup> and ArF<sup>(3)</sup> appear to be good candidates for high efficiency and high power and the mercury monohalide lasers of which HgCl<sup>(4)</sup> and HgBr<sup>(5)</sup> also appears to be good candidates. Although the spectra of these species have been excited in various ways they are not fully understood. Low pressure studies using either a flowing afterglow or e-beams generally exhibit broad spectra since the upper state is not vibrationally equilibrated. At high pressure using either e-beam or electric discharge excitation, the intense laser bands become significantly sharper and for cases where the lower state is bound the transitions to different vibrational levels of the ground state become resolved. These conditions are similar to those which result using high pressure laser mixtures. The e-beam or discharge approaches, however, have their limitations for certain kinetic studies. The main problem is the complexity added to the analysis due to the presence of large electron densities.

A new instrument is described here in which the upper levels of these laser systems may be populated by using photolytic pumping, at various pressures, in the absence of electrons.

This compact device can be of use in spectral and kinetic studies at gas temperatures up to several hundred degrees centigrade.

Measurements have been made, to date, on mercury chloride<sup>(6)</sup> and mercury bromide.<sup>(7)</sup> This paper will describe the experimental technique and its application to the measurement of mercury chloride kinetics. A more detailed analysis of these measurements will be presented elsewhere.

Excited mercury chloride is produced photolytically from mercuric chloride vapor

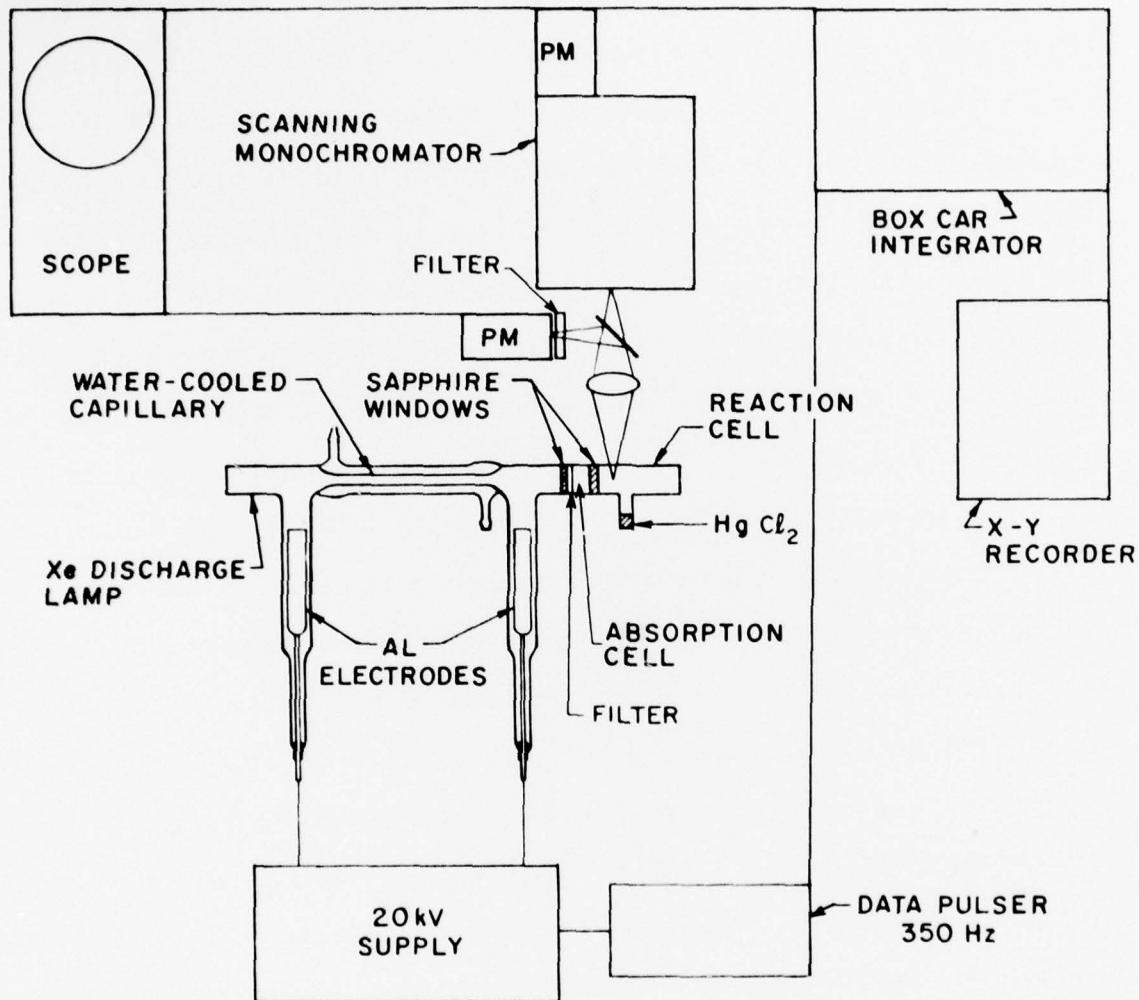


Wieland has examined<sup>(8)</sup> the excitation of the mercuric halides in detail and has determined that absorption at  $\lambda = 1810 \text{ \AA}$  maximizes production of  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ), while for mercuric bromide  $\lambda = 1950 \text{ \AA}$  maximizes  $\text{HgBr}^*$  ( $B^2\Sigma_{1/2}^+$ ). If on the other hand, one wished to produce  $\text{HgBr}^*$  C or D state then one could pump at  $1700 \text{ \AA}$  or  $1600 \text{ \AA}$ , respectively. Thus, the spectra and excited state kinetics of the various mercury halides, other metal halides and even the rare gas halide systems, all of which are of current laser interest are accessible for study in an electron free environment.

A schematic diagram of the experimental apparatus is shown in Figure 2. The reaction cell containing  $\text{HgCl}_2$  is heated in a dual oven arrangement. The reservoir portion of the cell is maintained at a temperature,  $T_1$ , which is typically  $\sim 90^\circ\text{C}$  providing a  $\text{HgCl}_2$  vapor pressure of  $\sim 50 \mu\text{m}$ . The main body of the cell is at a higher temperature,  $T_2 \sim 200^\circ\text{C}$ , to ensure that no mercuric chloride condenses on the sapphire cell window.

The Xe lamp is made of quartz with a sapphire output window similar in design to one described by Hoffman, Tanaka and Larrabee.<sup>(9)</sup> The lamp is drawn essentially to scale in Figure 2 in which the cooling jacket is 25 mm in diameter. Reliable operation is achieved using Al electrodes of 99.999% purity and evacuating the lamp and cell to the low  $10^{-7}$  torr range. The lamp is run with pure Xe at pressures between 150 torr and 250 torr much in the same way as described by Gedanken, et al.<sup>(10)</sup> The emission from the lamp in the vacuum ultraviolet is from  $Xe_2^*$  and peaked at 1750 Å, however, the lamp also emits throughout the ultraviolet and visible spectrum. Since the  $HgCl_2^*$  fluorescence signal of interest is also in the visible, the lamp background at these wavelengths is reduced by the use of a filter peaked at 1810 Å. For measurements on mercury bromide a filter peaked at 1950 Å has been used.

The Xe lamp is pulsed with 20 kV at  $\sim 350$  Hz with a pulse-width  $\sim 1$   $\mu$ sec. A schematic diagram showing the pulsing circuit is shown in Figure 3.  $HgCl_2^*$  fluorescence signals are detected either directly on a photomultiplier through an 80 nm bandpass filter to isolate the B + X emission bands or through a monochromator ( $\Delta\lambda = 6$  nm) as shown in Figure 2. The signals are averaged on a boxcar integrator (PAR Model 160) and displayed on an x-y recorder. Typical spectral data are shown in Figure 4. The top trace shows the observed  $HgCl_2^*$  emission obtained with 50  $\mu$ m pressure of  $HgCl_2$ . The time to sweep through such a spectrum is roughly 15 min. The bottom trace of Figure 4 shows a  $HgCl_2^*$  emission spectrum taken under conditions similar to the top trace but with 200 torr of Xe buffer gas added.



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Figure 2 Schematic Diagram of Experimental Apparatus for  $\text{HgX}^*$  Quenching Experiments

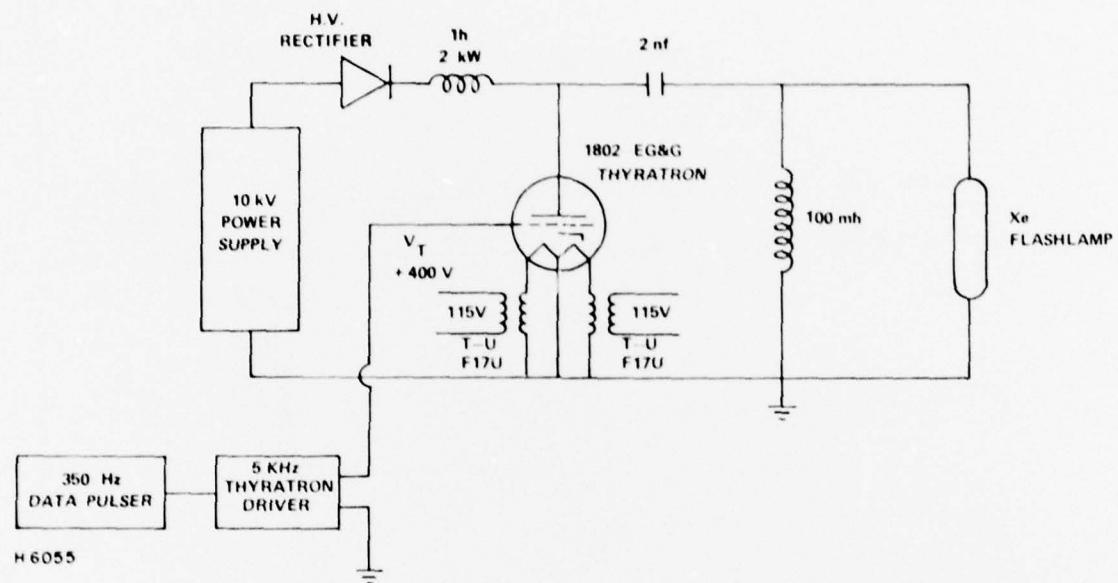


Figure 3 Schematic Diagram of Xe Flashlamp Pulse Circuit

HgCl\* EMISSION SPECTRA

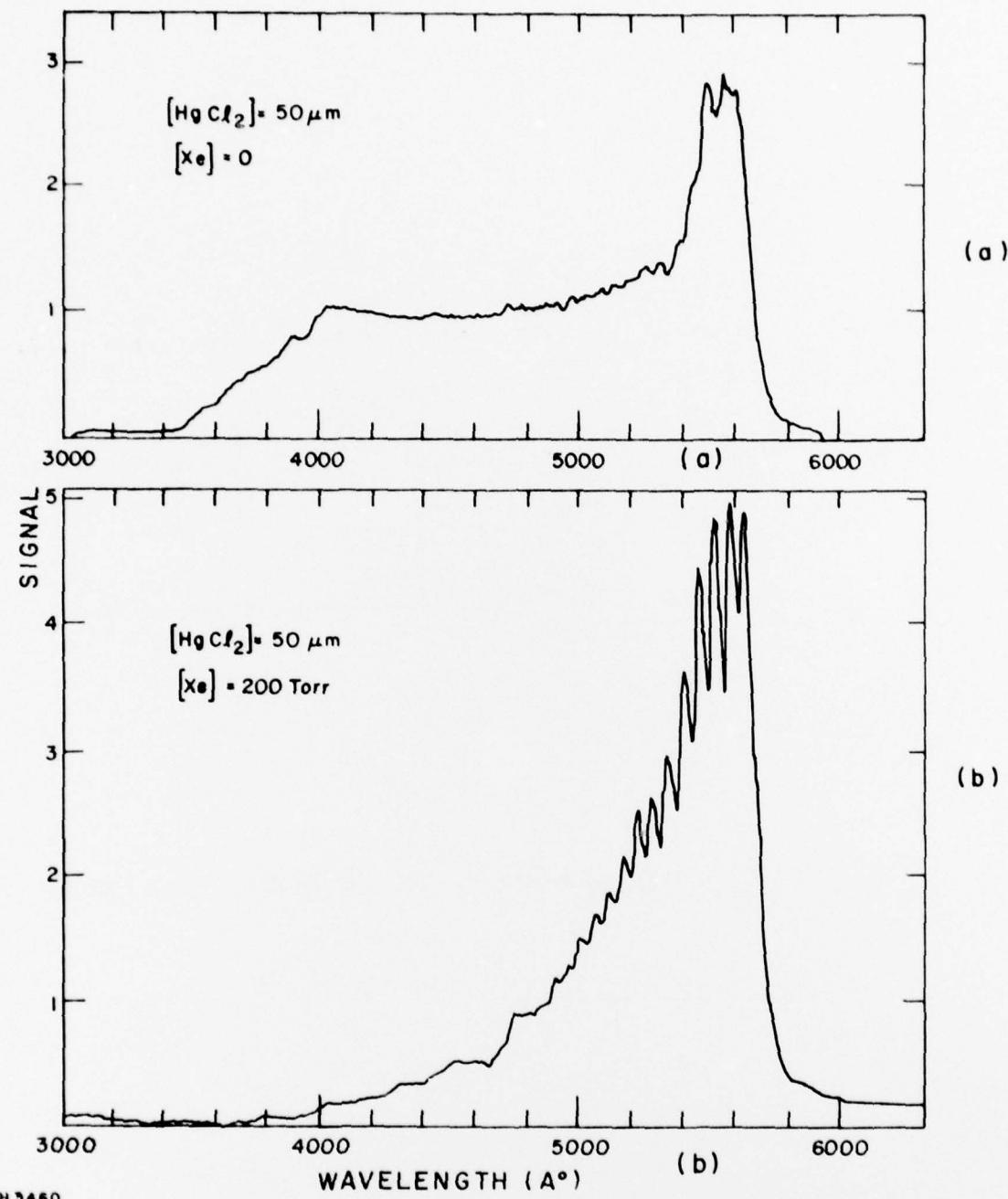


Figure 4a Measured HgCl\* Emission with  $[HgCl_2] = 50 \mu m$

4b Measured HgCl\* Emission with  $[HgCl_2] = 50 \mu m$  and  $[Xe] = 200 \text{ Torr}$ . The signal scale is the same as in Figure 4a.

Planimeter measurements of Figures 4a and 4b show comparable areas (total energy emitted) for these two cases which indicates negligible  $\text{HgCl}^*$  quenching at this Xe pressure. However, the dramatic change in the spectrum arises from the rapid relaxation of the  $\text{HgCl}^*$  vibrational levels by Xe. The significant difference between the two traces occurs because in the upper trace the  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) vibrational manifold is not relaxed so that emission from  $v' = 0, 1, 2, 3$  etc. is present and results in overlapping bands which broaden and diffuse the spectrum near 5600 Å. In addition a broad shoulder appears with significant contribution extending to roughly 3750 Å which is identified with transitions from  $B^2\Sigma_{1/2}^+$  levels  $v' \sim 20-25$  to  $X^2\Sigma_{1/2}^+$  levels  $v'' \sim 0-5$ . When Xe is added at pressures above 100 torr the upper vibrational manifold of  $\text{HgCl}^*$  ( $B^2\Sigma_{1/2}^+$ ) is relaxed. Thus, in Figure 4b the various vibrational transitions ( $0, v''$ ) are clearly defined with the most intense peak at  $v' = 0 \rightarrow v'' = 22$ . This prepares the initial state of the system more precisely and makes studies of, for example, quenching kinetics of  $B^2\Sigma_{1/2}^+$  ( $v' = 0$ ) straightforward.

In this optical pumping technique, the kinetics analysis can be complicated by the presence of quenching gas absorption at the pump wavelength. An absorption cell located between the lamp and reaction cell is used in additional experiments to measure the absorption cross sections of the various quenching gases at the excitation wavelength. In this experimental configuration the absorption at 1810 Å is measured by filling the absorption cell

with the quenching gas and monitoring the resulting decrease in  $\text{HgCl}^*$  fluorescence. Thus, we are able to make a measurement of a vacuum UV cross section, without the use of a vacuum UV monochromator, by observing a visible fluorescence signal. All the components between the lamp and the reaction cell are closely coupled to each other, minimizing intermediate air spaces and the resulting vacuum ultraviolet absorption by  $\text{O}_2$ . The end of the absorption cell closest to the reaction cell is apertured to a diameter of  $\sim 6$  mm by applying an Aquadag mask to reduce edge effects such as scattering.

A case in which the quenching molecule absorbs at the excitation wavelength ( $1810 \text{ \AA}$ ) is the quenching of  $\text{HgCl}^*$  by  $\text{HCl}$ . The quenching measurements were preceded by a determination of the  $\text{HCl}$  absorption cross section which was found to be  $\alpha_{\text{HCl}} \approx 9 \times 10^{-19} \text{ cm}^2$ . This cross section agrees with the work of Myer and Samson<sup>(11)</sup> within the experimental uncertainty and will be discussed in detail elsewhere.

### III. TWO BODY COLLISIONAL QUENCHING KINETICS OF $\text{HgCl}^*$ ( $B^2\Sigma$ )

Laser action has been achieved on the mercury monohalides by pure e-beam pumping,<sup>(4,5)</sup> electric discharges,<sup>(12,14)</sup> and also photolytic pumping.<sup>(15)</sup> In order to optimize the efficiency of these laser systems, a detailed knowledge of the heavy-particle quenching kinetics is important. In this paper, we report measurements of the quenching rate of  $\text{HgCl}^*$  by He, Ar, Xe,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{HCl}$ , and  $\text{CCl}_4$ . These rates were obtained by analyzing the steady-state dependence of the  $\text{HgCl}^*$  fluorescence intensity on the partial pressure of the quenching gas.

Mercury chloride is produced in the excited state,  $B^2\Sigma_{1/2}^+$ , by optically pumping  $\text{HgCl}_2$  vapor,<sup>(16)</sup> at  $\lambda = 1810 \text{ \AA}$ , which reduces the possibility of producing other excited  $\text{HgCl}$  species. Spontaneous emission from excited  $\text{HgCl}^*$  molecule in the  $B \rightarrow X$  bands is used to monitor the excited state density. The radiative lifetime of  $\text{HgCl}^*$  has been recently calculated by Duzy and Hyman<sup>(17)</sup> as 20 nsec. Considering the uncertainties in this calculation, we have normalized their results to the measured  $\text{HgBr}^*$  lifetime<sup>(18)</sup> of 23 nsec and estimate the radiative lifetime of  $\text{HgCl}^*$  as  $\tau = 29 \text{ nsec.}$

A modified Stern-Volmer analysis has been applied to the variation of emission intensity with pressure of the additive gas to determine the quenching rate constants for various gases

quenching  $\text{HgCl}^*$ . This optical pumping technique avoids any ambiguities which might be introduced by the presence of electrons.

A schematic diagram of the experimental apparatus is shown in Figure 2. The reaction cell containing  $\text{HgCl}_2$  is heated in a dual-oven arrangement. The reservoir portion of the cell is maintained at a temperature  $T_1$  which is typically  $\sim 90^\circ\text{C}$  providing a  $\text{HgCl}_2$  vapor pressure of  $\sim 50 \mu\text{m}$ . The main body of the cell is at a higher temperature,  $T_2 \sim 200^\circ\text{C}$ , to ensure that  $\text{HgCl}_2$  does not deposit on the sapphire cell window. The Xe lamp is similar in design to one described by Hoffman, Tanaka, and Larrabee<sup>(9)</sup> but it is made of quartz and has a sapphire output window. This lamp pulsed at  $\sim 350$  Hz with pure Xe at pressures between 150 and 250 torr similar to the lamp described by Gedanken et al.<sup>(10)</sup> Thus, the emission from the lamp in the vacuum ultraviolet is from  $\text{Xe}_2^*$  and is peaked at  $1750 \text{ \AA}$ ; however, the lamp also emits throughout the ultraviolet and visible spectrum. A 36 nm bandpass filter peaked at  $1810 \text{ \AA}$  selects the  $\text{HgCl}^*$  excitation wavelength and reduces the visible light background in the region of  $\text{HgCl}^*$  fluorescence. An absorption cell located between the lamp and reaction cell is used in additional experiments to measure the absorption cross sections of the various quenching gases at the excitation wavelength. In this experimental configuration the absorption at  $1810 \text{ \AA}$  is measured by filling the absorption cell with quenching gas and monitoring the resulting decrease in  $\text{HgCl}^*$  fluorescence.

The  $\text{HgCl}^*$  fluorescence signals are detected either directly on a photomultiplier tube using a 80-nm bandpass filter to isolate the  $B \rightarrow X$  emission bands or through a monochrometer as shown in Figure 2. The signals are averaged on a boxcar integrator (PAR Model 160) and displayed on an x-y recorder. The top trace [Figure 4a] shows the observed  $\text{HgCl}^*$  emission obtained with 50  $\mu\text{m}$  pressure of  $\text{HgCl}_2$ . Figure 4b shows an  $\text{HgCl}^*$  spectrum taken under similar conditions but with 200 torr of Xe buffer gas added. Planimeter measurements show comparable areas (total energy emitted) for these two cases which indicates negligible  $\text{HgCl}^*$  quenching. The dramatic change in the spectra arises from the rapid relaxation of the  $\text{HgCl}^*$  vibrational levels by Xe. In the upper trace the  $\text{HgCl}^*$  vibrational manifold is not relaxed so that emission from  $v' \geq 0$  is present and results in overlapping bands which broaden and diffuse the spectrum near 5600 Å. This suggests that high vibrational levels of the B state are produced in the photodissociation of  $\text{HgCl}_2$ . In Figure 4b, the excited state vibrational levels are relaxed and vibrational transitions from  $v' = 0$  are clearly observed with the most intense peak at  $v' = 0 \rightarrow v'' = 22$ . Several spectra were taken at varying Xe pressures and indicated that  $B^2\Sigma$  state is vibrationally relaxes at Xe pressures of roughly 100 torr. The fluorescence spectrum in Figure 4b is similar to that observed in  $\text{HgCl}^*$  laser experiments<sup>(4)</sup> which used a 3-amagat Ar/Xe laser gas mix. All the quenching data presented below were taken with at least 100 torr of Xe present to ensure that electronic quenching of the upper laser level,  $v'' = 0$ , was being observed. The quenching by Xe will be shown to be negligible under these conditions.

The rate equation governing the density of the excited mercury chloride,  $[\text{HgCl}^*]$ , yields the steady state  $\text{HgCl}^*$  emission signal

$$S_Q = \frac{[\text{HgCl}^*]_Q}{\tau} = \frac{\exp(-\alpha) \Lambda}{1 + \frac{k_Q [Q] \tau}{k' [\text{HgCl}_2] \tau}} \quad (2)$$

Here  $\alpha = [Q] \sigma_Q \ell$ , where  $\sigma_Q$  is the absorption coefficient of the quenching molecule,  $Q$ , at the excitation wavelength, and  $\ell$  is the absorption path length. The numerator is proportional to  $\Lambda$ , the source term for production of  $\text{HgCl}^*$  which depends linearly on pump intensity. This source term is thus reduced by the exponential for cases where the quenching molecule absorbs at the excitation wavelength. We now define the ratio of the fluorescence signal without quenching to the signal  $S_Q$ .

$$R = \exp(-\alpha) \left\{ 1 + \frac{k_Q [Q]}{1/\tau + k' [\text{HgCl}_2]} \right\} \quad (3)$$

The density of  $\text{HgCl}_2$  typically used in these experiments is  $1.5 \times 10^{15} \text{ cm}^{-3}$  and even if we assume  $k'$  has a gas kinetic rate ( $k' = 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ ) we have  $1/\tau \gg k' [\text{HgCl}_2]$  for  $\tau = 29 \text{ nsec}$ . Thus to a good approximation  $R \exp(-\alpha) = 1 + k_Q [Q] \tau$  and we can use a modified Stern-Volmer analysis which plots  $R \exp(-\alpha)$  vs  $[Q]$  resulting in a straight line with slope  $k_Q \tau$ . Since the rare gases do not absorb light at the excitation wavelength,  $\alpha = 0$ , and the standard Stern-Volmer expression results.

The possibility of a relatively long-lived (1-10 nsec) intermediate excited state  $\text{HgCl}_2^*$  which could be quenched prior to

dissociation has been considered. Spectroscopic studies of the photodissociation of the mercury dihalides<sup>(19,20)</sup> as well as recent laser photolysis<sup>(15)</sup> of  $\text{HgBr}_2$  do not exhibit evidence of such intermediate states. This is consistent with the possibility of numerous curve crossings in the excited states of these triatomics suggested by recent analysis<sup>(21)</sup> of the potential energy surfaces of  $\text{HgI}_2$ . Consequently, we will assume that the photodissociation is instantaneous in the analysis.

Measurements were made of the quenching of  $\text{HgCl}^*$  by several of the rare gases and  $\text{N}_2$ . He, Ar, and  $\text{N}_2$  showed no measurable quenching of the electronic state of  $\text{HgCl}^*$  over the pressure range (0-1000 torr). This leads to an upper bound for these quenching rates of  $5 \times 10^{-14} \text{ cm}^3/\text{sec}$  when one takes into account the sensitivity of the experiment and the overall uncertainties of the measurement. The only measurement in the literature to which one might compare is the work of Tibilow<sup>(22)</sup> which reports no observed quenching of  $\text{HgCl}^*$  by  $\text{N}_2$ . The only rare gas studied here in which quenching was observed was Xe for which we determined  $k_{\text{Xe}}\tau = 6.9 \times 10^{-21} \text{ cm}^{-3}$ . The observed pressure dependence of the data suggests that this is a two-body process and assuming  $\tau = 29 \text{ nsec}$ , the two body quenching rate constant is  $k_Q = 2.4 \times 10^{-13} \text{ cm}^3/\text{sec}$ . A new high-pressure cell is being constructed in which three-body quenching and the effects of Hg on  $\text{HgCl}^*$  can be examined.

A case in which the quenching molecule absorbs at the excitation wavelength 1810 Å is shown in Figure 5. The quenching measurements were preceded by a determination of the HCl absorption cross section which was found to be  $\alpha_{HCl} \approx 9 \times 10^{-19} \text{ cm}^2$ . This cross section agrees with the work of Myer and Samson<sup>(11)</sup> and will be discussed in detail elsewhere.<sup>(7)</sup> The slope determined from the data of Figure 5 results in a value  $k_{HCl} \tau = 2.5 \times 10^{-18} \text{ cm}^3$  which corresponds to a quenching rate constant  $k_Q = 8.6 \times 10^{-11} \text{ cm}^3/\text{sec}$  assuming  $\tau = 29 \text{ nsec}$ . Quenching rate constants were also measured for  $CCl_4$  and  $Cl_2$  which were used as Cl donors in previous e-beam-pumped and discharge-pumped lasing experiments. The measured values of the product  $k_Q \tau$  for the various atoms and molecules are listed in Table III and we have also deduced the quenching rate constants assuming  $\tau = 29 \text{ nsec}$ . The overall uncertainty in these measurements is  $\pm 25\%$ . Although the lifetime has not been accurately determined for  $HgCl^*$ , it has been shown<sup>(23)</sup> that important laser parameters such as fluorescence efficiency and saturation flux depend only on the measured product of the quenching rate and upper state lifetime.

Using the quenching rates given above, an estimate of the saturation flux can be obtained for arbitrary mixtures of Ar/Hg/ $Cl_2$  and Ar/Xe/Hg/ $CCl_4$  which have been used respectively in discharge pumping and e-beam pumping of the  $HgCl^*$  laser. The measurement of Hg quenching of  $HgCl^*$  is in progress and here we estimate this quenching rate constant to be  $k_Q = 2 \times 10^{-11} \text{ cm}^3/\text{sec}$

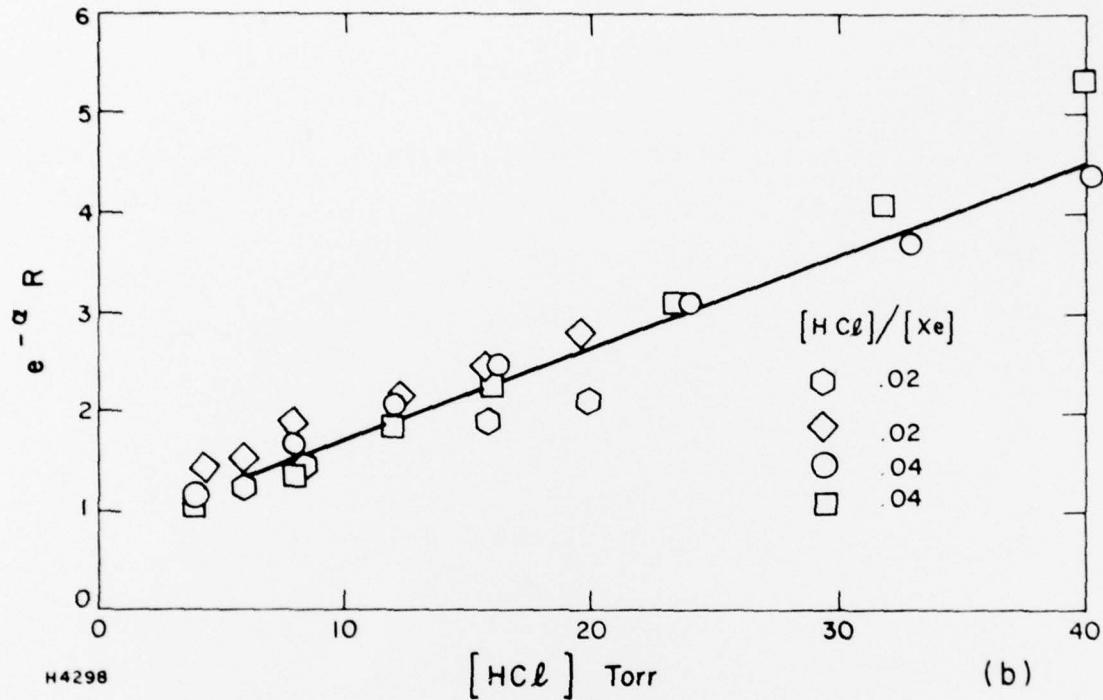


Figure 5 Measured Data for  $\text{HCl}$  Quenching  $\text{HgCl}^*$ . The  $\text{HCl}$  was added as a 2% and 4% mix in  $\text{Xe}$ . At the higher  $\text{HCl}$  pressure the  $\text{Xe}$  pressure is up to 1000 Torr. The small effect of  $\text{Xe}$  quenching the  $\text{HgCl}$  has been accounted for.

TABLE III  
 HgCl\* QUENCHING  
 (Assuming  $\tau_{\text{HgCl}*} = 29 \text{ nsec}$ )

<u>Q</u>	<u><math>k_{Q\tau}</math></u> ( $\text{cm}^3$ )	<u><math>k_Q(\text{HgCl}*)</math></u> ( $\text{cm}^3/\text{sec}$ )
He	$< 1.5 \times 10^{-21}$	_____
Ar	$< 1.5 \times 10^{-21}$	_____
Xe	$6.9 \times 10^{-21}$	$2.4 \times 10^{-13}$
N <sub>2</sub>	$< 1.5 \times 10^{-21}$	_____
C <sub>2</sub>	$3.8 \times 10^{-18}$	$1.3 \times 10^{-10}$
HC	$2.5 \times 10^{-18}$	$8.6 \times 10^{-11}$
CC <sub>4</sub>	$3.5 \times 10^{-18}$	$1.2 \times 10^{-10}$

which is comparable to the rate constant of ArF\* quenching by Ar<sup>(24)</sup> and XeF\* quenching by Xe.<sup>(25)</sup> The saturation flux  $\phi_s$  can be computed using the following expression.<sup>(26)</sup>

$$\phi_s = \frac{hv}{\sigma_s \tau} (1 + K_{\text{Ar}} [Ar] + K_{\text{Ar}} [Ar] \\ + K_{\text{Xe}} [Xe] + K_{\text{Hg}} [Hg]), \quad (4)$$

where  $\sigma_s$  is the stimulated cross section,  $hv$  is the photon energy,  $\tau$  is the HgCl\* radiative lifetime, and  $K_i$  the quenching rate constant for each gas component. It should be noted that the saturation flux defined above is applicable in the limit that the population of the lower laser is negligible. From the HgCl\* spontaneous spectra<sup>(4)</sup> we have estimated  $hv/\sigma_s \tau$  to be  $0.035 \text{ MW/cm}^2$ . For typical laser mixes containing 1% Cl<sub>2</sub>, 2% Hg, and 97% Ar at a total pressure of 2 amagats and 1% CCl<sub>4</sub>, 2% Hg, 11% Xe, and 86% Ar at a similar total pressure, one obtains  $\phi = 0.12 \text{ MW/cm}^2$ .

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